

# Sum Frequency Generation (SFG) Studies on Molecular Structure at Octadecyltrichlorosilane modified Fused Quartz / Solution Interfaces

S. Nihonyanagi, S. Ye and K. Uosaki

Division of Chemistry, Graduate School of Science,  
Hokkaido University, Sapporo 060-0810, JAPAN

## INTRODUCTION

Interfacial water molecules play prominent roles in many physical, chemical and biological processes. Although many theoretical studies on the structure of water molecules at various interfaces are available, most of the experimental investigations on the water structure have been carried out mainly in vapor or bulk aqueous phase due to a lack of effective experimental probe for interfacial study. Recently, sum frequency generation (SFG) spectroscopy has been widely employed to study the structure of water at various interfaces by some research groups.

A number of reviews have been published about the theory background of SFG and its application<sup>1</sup>. As a second-order nonlinear optical process, SFG is forbidden in a medium with inversion symmetry and is only active at an interface where the inversion symmetry is broken. In the infrared-visible SFG spectroscopy, one can obtain vibrational spectra of various interfaces.

We carried out the SFG studies of water structure at a fused quartz surface modified with amino terminated self-assembled monolayers (SAMs), N-(2-amino-ethyl)-3-aminopropyl-methoxysilane (AAS) and 3-aminopropyl-methoxysilane (APS), in phosphate buffer solutions of various pHs and ionic strengths and found that both terminal amino group and silanol group on the quartz substrate have great effects on the SFG signals from the interfacial water molecules<sup>2-3</sup>. However, it was found that AAS or APS SAMs with high coverage were difficult to prepare on the fused quartz surface by silane coupling reaction. OTS has been known to form an ideal SAM on the quartz surface and is expected to have no pH effect on the water structure due to the methyl terminal group. Thus, the SFG study on the water structure at the OTS modified quartz / solution interface can provide essential information to understand the structure of water molecules on the SAM/solution interface.

In this work, we investigate the pH dependent structure of water molecules at the fused quartz/ OTS/ solution interface by *in situ* SFG measurements.

## EXPERIMENTAL

A picosecond infrared-visible SFG system used in this study has been described elsewhere<sup>2</sup>. Tunable infrared radiation from 2.3 to 8.5  $\mu\text{m}$  was generated by OPG/OPA/DFG system pumped by a Nd:YAG laser. 532nm was used as visible light. The infrared and visible beams were focused on the same point of the sample surface with incident angle of 70 and 50 degrees, respectively.

The surface of a thoroughly cleaned fused quartz prism was modified by octadecyltrichlorosilane ( $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ ; OTS) using silane coupling reaction. The *in situ* SFG measurements were carried out in phosphate buffer solutions with controlled pH and ionic strength (I).

## RESULTS

Figure 1 shows SFG spectra (black dots) of OTS SAM on the fused quartz in the phosphate buffer solutions of different pH (I=10 mM) in the region of 2800 ~ 3800  $\text{cm}^{-1}$ . Polarization combinations of SFG, visible and IR lights were *s*, *s* and *p*, respectively. The solid lines show the theoretical fits using five resonance bands. Two strong sharp peaks were observed at 2880 and 2940  $\text{cm}^{-1}$  at all pH and were assigned to the C-H symmetric stretching of  $\text{CH}_3$  group of OTS and the Fermi Resonance, respectively. In the O-H stretching region, the intensities and shape of SFG spectra changed dramatically with pH. In the solution of neutral pH (Fig.1b), the shape of the spectrum was nearly the same as the SFG spectrum of OTS / water interface reported by Du et al<sup>4</sup>. A broad band at 3200  $\text{cm}^{-1}$  and a shoulder at 3400  $\text{cm}^{-1}$  were observed, which can be assigned to the symmetric O-H stretching of tetrahedrally and asymmetrically coordinated water molecules, respectively. The fact that the band at 3200  $\text{cm}^{-1}$  is much stronger than the band at 3400  $\text{cm}^{-1}$  indicates that the interfacial water is well ordered. A sharp peak at 3680  $\text{cm}^{-1}$  is assigned to the OH stretching of the dangling OH of the first water layer.

In the alkaline solution (Fig. 1a), the intensity of the SFG spectra was much higher than that in the solution of pH = 7. The shape of the SFG spectrum at pH = 2, was completely different from that of Figs. 1a and 1b as shown in Fig. 1c.

The structure of the OTS SAM and the interfacial water in the solution of various pH will be discussed based on these SFG spectra.

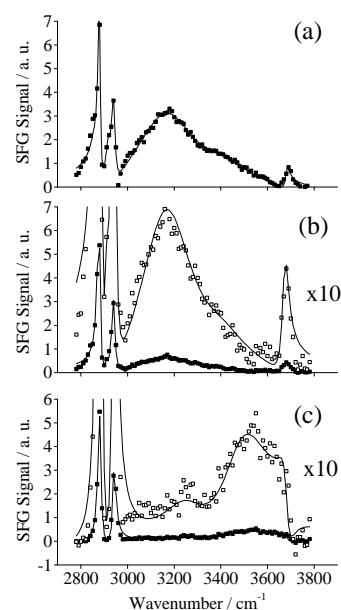


Fig. 1 SFG spectra of quartz / OTS / phosphate solution interface. pH of the bulk solutions (a), (b), (c) is 11, 7, 2, respectively.

## Reference

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